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METHOD FOR VAPOR-DEPOSITING A SUBSTRATE WITH A NEEDLE-SHAPED X-RAY FLUORESCENT MATERIAL, AND X-RAY FLUORESCENT MATERIAL

5 The invention concerns a method for vapor deposition of a substrate with a layer of a spicular x-ray luminophore with at least one alkali metal as well as the x-ray luminophore. X-ray luminophore is thereby to be viewed as a "place holder" for scintillator with fluorescence and storage luminophore with emission via stimulation with laser light. By fluorescence, what is generally understood is the
10 excitation of a luminophore with high-energy radiation (UV, x-ray) under emission of low-energy radiation (emission). In the storage luminophore, higher-energetic emission (for example 420 nm) is triggered with low-energetic radiation (for example 680 nm) since the "residual energy" in the x-ray has been "stored".

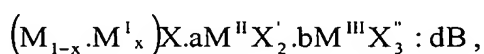
15 X-ray luminophores are generally used in medical technology and destruction-free material testing. In these applications, on the one hand scintillators with spontaneous emission under x-ray excitation are used, and on the other hand storage luminophores with formation and storage of electrons and holes with subsequent photo-stimulated emission (PSL) upon irradiation with, for example,
20 red light are used. The x-ray luminophores based on alkali halogenide thereby assume a very particular role. Examples for this are CsI:Na in the x-ray intensifier, CsI:Tl in a-Si detectors or, of late, CsBr:Eu as a storage luminophore plate as it is, for example, described in Proc. of SPIE Vol. 4320 (2001), "New Needle-crystalline CR Detector" by Paul J. R. Leblans et al., pages 59 through 67.

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In all cited medical applications of alkali halogenide it is common that on the one hand a high x-ray absorption must ensue to achieve a high DQE in the alkali halogenide layer, and on the other hand the signal (light) must be clear over the noise. A high x-ray absorption is achieved by an approximately 500 – 600 μm
30 thick alkali halogenide layer. The problem of a still-too-low light yield is still

present in all cited medical applications. In particular the lacking light yield of the storage luminophore represents a problem that is still not completely solved.

In US 5,028,509, example 14 it is described how the CsBr:Eu used there as a
5 storage luminophore is produced from CsBr and Eu₂O₃. The general formula for the combination of the alkali halogenide luminophore (Cs and Br) is specified as follows:



whereby M = Cs or Rb, M^I is at least one alkali metal from the group Li, Na, K, Rb
10 and Cs, M^{II} is at least one bivalent metal from the group Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu and Ni, M^{III} is at least one metal from the group Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga and In, B is an activator that is at least one metal from the group Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu, Mg, Pb, Bi, Mn and In, X, X' and X'' are the same or
15 different and represent a halogen atom from the group F, Cl, Br and I.

Known from WO 01/03156 A1 is a production method for a stimulatable storage
luminophore of the general formula CsX : Eu for the combination of the
luminophore for the Cs-bromide and/or -chloride. Such a storage luminophore
20 was produced from CsBr and EuBr₂, EuBr₃ or EuOBr.

In EP 1 113 458 A1, a method is described for coating a substrate in which Eu is introduced as EuX₂, EuX₃, and EuOX.

25 All of these luminophores have in common that the doping material is a relatively simple molecule. These simple molecules are often attached on interstitials.

In tests with storage luminophore powders, it has been shown that microscopically small phases of the doping material can be formed in the alkali halogenide. In
30 vacuum-deposited layers of CsBr:Eu, these phases have not been found before. On the one hand, this is due to the Eu concentration in the layer being only maximally

3000 ppm (0.3 mol%), conditional upon production (different vapor pressures of CsBr and EuBr₂), while given the use of powder phases and an optimal PSL signal were only present given Eu concentrations >1 mol%.

- 5 The invention originates from the object to fashion an x-ray luminophore as well as a method for production of a spicular x-ray luminophore, such that an optimal light yield can be achieved.

The object is inventively achieved with regard to the method in that alkali
10 halogenide phases are simultaneously vaporized with an alkali halogenide, mixed in the vapor phase and vacuum-deposited on the substrate. The use thereby already begins upon coating of the vaporizer with evaporating material. The vaporization of the phase is to be learned from none of the literature cited above; rather, a formation of the phase in the layer is to be learned.

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It has proven to be advantageous when the vaporization is implemented at temperatures between 50° C and 300°C and a pressure between 0.001 Pa and 3 Pa.

A better distribution of the evaporated phases and increase of the light yield is
20 obtained when a temperature treatment of the luminophore layer is implemented after the vaporization and a cooling, whereby the temperature treatment after cooling preferably ensues at room temperature in the presence of water vapor.

The temperature treatment can inventively ensue in the range of 100°C to 300°C in
25 environment air or an inert gas.

In an advantageous manner, Cs_xEu_yBr_(x+2y) can be used as an alkali halogenide phase and CsBr can be used as an alkali halogenide, such that a x-ray storage luminophore of the general formula CsBr: Cs_xEu_yBr_(x+2y) forms.

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It has proven to be advantageous when a quantity x of the alkali halogenide phase and a quantity (600g -x) of the alkali halogenide are mutually vaporized.

5 The substrate, with the layer of the spicular x-ray luminophore, can inventively form a storage luminophore plate.

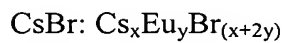
For inventive mixing, the alkali halogenide phase and the alkali halogenide can be mixed in the vaporization phase and in a vaporization boat, or the alkali halogenide phase and the alkali halogenide can be separately introduced in a plurality of
10 vaporization boats.

The object is inventively achieved for the x-ray luminophore in that it is produced according to the following formula:

$$\left(\left(M^{+} H^{-} \right)_a \left(M^{++} H^{-} \right)_{(1-a)} \right)_k : \left(M^{+} S^{z+} H^{-} H^{'''-z+y} \right)_b \left(M^{++} S^{z+} H^{-} H^{'''-z+y} \right)_c$$
$$15 \left(M^{+} S^{z+} H^{-} H^{'''-z+y} \right)_d \left(M^{++} S^{z+} H^{-} H^{'''-z+y} \right)_e$$

whereby M^{+} is at least one metal ion from the group Na, K, Rb and Cs, H^{-} is at least one halogenide from the group F, Cl, Br and I and S^{z+} is at least one lanthanide ion from the group La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er,
20 Tm, Yb or Lu.

Particularly advantageous is an x-ray storage luminophore according to the following formula:



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The invention is now based on the idea to produce the alkali halogenide phases and to vaporize these simultaneously with an alkali halogenide. The vaporization can thereby ensue from a vaporization boat or from two or more vaporization boats. A temperature treatment of the storage luminophore, implemented after the

vaporization and cooling, leads to a better distribution of the evaporated phases and thus increases the light yield by a factor of 2 – 10, typically by a factor of 4 – 5.

5 Tests have shown that the temperature treatment is effective only after cooling to room temperature given simultaneous presence of water vapor. The water vapor can both be added, for example, to an inert gas Ar, N₂, He, Ne, Kr or also be in the environment air. A direct high heating – also after cooling after the vaporization – has as a consequence no improvement of the light yield. The layer must thus initially “have seen water vapor”.

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Spicular layers that enable a homogenous distribution of the phase material in the alkali halogenide are created upon vaporization conditional upon the pressure and temperature control. As a consequence of this, 100 – 800 ppm of the phase material (average value above the layer thickness) is already sufficient in order to
15 achieve an optimal light yield.

In vaporization, temperatures are set between 50°C and 300°C and pressures are set between 0.001 Pa and 3 Pa. The temperature given subsequent tempering is advantageously as high as the average substrate temperature was upon
20 vaporization.

The tempering time is selected such that the desired light yield is achieved.

25 As a result of this mixture made from alkali halogenide and alkali halogenide phase in the vaporization phase, a new spicular luminophore type is produced that can be described with chemical formulas as follows.

Via the formation of a phase Cs_xEu_yBr_(x+2y) in CsBr, a storage luminophore with very high light yield results of the combination:

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The general formula for the M^+ alkali halogenides Na, K, Rb and Cs as well as H⁻ halogenides F, Cl, Br and I reads:

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$$M'^+H'^- : M'^+_x Eu_y H'^-{}_x H''^-{}_{2y}, \text{ (also possible: } \dots H''^-{}_x H'^-{}_{2y})$$

whereby the halogenides H'^- and H''^- can be the same or different.

- 10 Two (or more) alkali halogenides can also be used as a matrix lattice; the general sum formula then reads:

$$(M'^+ H'^-)_a (M''^+ H''^-)_{(1-a)} : M'^+_x Eu_y H'^-{}_x H''^-{}_{2y},$$

whereby the alkali halogenides M'^+ and M''^+ can be the same as well as different.

- 15 Likewise, the halogenides H'^- , H''^- and H'''^- can be the same or different.

According to the above configuration, other phases are also conceivable:

$$(M'^+ H'^-)_a (M''^+ H''^-)_{(1-a)} : M'^+_x Eu_y H'^-{}_x H''^-{}_{2y},$$

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and

$$(M'^+ H'^-)_a (M''^+ H''^-)_{(1-a)} : M'^+_x Eu_y H'^-{}_x H''^-{}_{2y} \\ M''^+_x Eu_y H''^-{}_x H'''^-{}_{2y},$$

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and generalized:

$$(M'^+ H'^-)_a (M''^+ H''^-)_{(1-a)} : (M'^+_x Eu_y H'^-{}_x H''^-{}_{2y})_b (M''^+_x Eu_y H''^-{}_x H'''^-{}_{2y})_c \\ (M'^+_x Eu_y H''^-{}_x H'''^-{}_{2y})_d (M''^+_x Eu_y H'^-{}_x H'''^-{}_{2y})_e$$

(or also without H''', only made of H'', H'''), whereby a can be equal to 1, b, c, d and e can be equal to 0, and H'', H''' and H'''' can be the same or different.

- 5 Instead of Eu^{2+} , other lanthanides S^{z+} from the group La, Ce, Pr, Nd, Pm, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu can also be used. The corresponding general formula then reads:

$$\left(\left(\text{M}^{i+} \text{H}^{j-} \right)_a \left(\text{M}^{i'+} \text{H}^{j'-} \right)_{(1-a)} \right)_k : \left(\text{M}^{i+} \text{S}^{z+} \text{H}^{j-} \text{H}^{i''-} \text{H}^{j''-} \right)_b \left(\text{M}^{i'+} \text{S}^{z+} \text{H}^{j'-} \text{H}^{i'''-} \text{H}^{j'''-} \right)_c$$

$$10 \quad \left(\text{M}^{i+} \text{S}^{z+} \text{H}^{j'-} \text{H}^{i''-} \text{H}^{j''-} \right)_d \left(\text{M}^{i'+} \text{S}^{z+} \text{H}^{j'-} \text{H}^{i'''-} \text{H}^{j'''-} \right)_e$$

The factor k can also be 0, such that "pure" phase material is obtained.

- 15 Both scintillators (luminophores) and storage luminophores are contained under the cited x-ray luminophores.

Some exemplary embodiments for production of the inventive luminophore are subsequently specified:

- 20 a) 50 g CsEuBr_3 are mixed with 550 g CsBr, and subsequently a storage luminophore $\text{CsBr: Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- b) 20 g CsEu_2Br_5 are mixed with 580 g CsBr, and subsequently a storage luminophore $\text{CsBr: Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- 25 c) 100 g CsEu_3Br_7 are mixed with 500 g CsBr, and subsequently a storage luminophore $\text{CsBr: Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.

- d) 10 g Cs_2EuBr_4 are mixed with 590 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- 5 e) 10 g Cs_3EuBr_5 are mixed with 590 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- f) 100 g Cs_4EuBr_6 are mixed with 500 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- 10 g) 30 g $\text{Cs}_2\text{Eu}_2\text{Br}_6$ are mixed with 570 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- h) 70 g $\text{Cs}_3\text{Eu}_2\text{Br}_7$ are mixed with 530 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- 15 i) 35 g $\text{Cs}_3\text{Eu}_3\text{Br}_9$ are mixed with 565 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- j) 25 g CsEuBr_3 and 25 g $\text{Cs}_2\text{Eu}_2\text{Br}_6$ are mixed with 550 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- 20 k) 15 g CsEuBr_3 and 25 g $\text{Cs}_3\text{Eu}_3\text{Br}_9$ are mixed with 560 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- 25 l) 20 g CsEuBr_3 and 10 g CsEu_2Br_5 are mixed with 570 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
- m) 10 g CsEuBr_3 and 40 g CsEu_3Br_7 are mixed with 550 g CsBr, and subsequently a storage luminophore CsBr: $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ (spicular) is produced with the typical vacuum-deposition method.
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- n) 30 g CsEuBr₃ and 20 g Cs₂EuBr₄ are mixed with 550 g CsBr, and subsequently a storage luminophore CsBr: Cs_xEu_yBr_(x+2y) (spicular) is produced with the typical vacuum-deposition method.
- o) 60 g CsEuBr₃ and 20 g Cs₃EuBr₅ are mixed with 520 g CsBr, and subsequently a storage luminophore CsBr: Cs_xEu_yBr_(x+2y) (spicular) is produced with the typical vacuum-deposition method.
- p) 40 g CsEuBr₃ and 20 g Cs₃Eu₂Br₇ are mixed with 540 g CsBr, and subsequently a storage luminophore CsBr: Cs_xEu_yBr_(x+2y) (spicular) is produced with the typical vacuum-deposition method.

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Other mixtures made up of two materials of the Cs₂... and Cs₂... compounds and Cs₂... and Cs₃ or Cs₄... compounds – as have been shown in the example Cs... - can also be used for production of the storage luminophores. Other quantity, mixture and concentration ratios of 0.1 mol% - 20 mol% are also suitable for the production of storage luminophore. Mixtures made from not only two materials, but rather made from three, four... materials are also suitable as a basis for a storage luminophore.

If a non-vaporizable residue remains in the vaporization boat, normally CsBr: Cs_xEu_yBr_(x+2y), pure CsBr can also be refilled and subsequently this mixture can be vaporized. This can also ensue multiple times until the CsBr: Cs_xEu_yBr_(x+2y) concentration has fallen under 0.1 mol%.

Instead of a mixture, the individual substances Cs_xEu_yBr_(x+2y) and CsBr can also be vaporized from two or more vaporization boats. CsBr and Cs_xEu_yBr_(x+2y) can also be vaporized as a mixture from one vaporization boat and be vaporized from a different one pure substance, for example CsBr.

A europium/bromine compound (for example EuBr₂, EuBr₃) can also be vaporized together with the Cs_xEu_yBr_(x+2y) and CsBr. Instead of the bromides, fluorides, chlorides and/or iodides can also be used.

Europium oxibromides (for example EuOBr , $\text{Eu}_3\text{O}_4\text{Br}$, Eu_3OBr_4 , Eu_4OBr_6) can also be vaporized together with the $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ and CsBr . Instead of the oxybromides, oxyfluorides, oxychlorides and/or oxyiodides can also be used.

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Europium oxides (for example EuO , Eu_2O_3) can also be vaporized together with the $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ and CsBr .

10 Europium oxibromide and europium oxide can also be vaporized together with the $\text{Cs}_x\text{Eu}_y\text{Br}_{(x+2y)}$ and CsBr .

Instead of the specified cesium, other alkaline metals (Na, K, Rb) and all halogenides (F, Cl, Br, I) can also be used in the mixtures corresponding to the illustrated general sum formulas.

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Via the doping of an alkali halogenide with an alkali halogenide-rare earth phase, a novel spicular luminophore type has been produced that is superior to the previously known luminophore types in terms of its light yield. Depending on the luminophore combination, both scintillators and storage luminophores can thereby

20 be created.